



Short communication

Electrochemical behavior of carbon-coated silicon monoxide electrode with chromium coating in rechargeable lithium cell



Sun Woo Hwang, Jun Kyu Lee, Woo Young Yoon*

Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong, Sungbuk-Gu, Seoul 136-701, Republic of Korea

HIGHLIGHTS

- Chromium is coated onto the silicon monoxide carbon composite electrode through ion beam sputter.
- Capacity of the coated cell was 1127 mAh g⁻¹ at the first while that of the uncoated cell is 956 mAh g⁻¹.
- The capacity retention ratio of the Cr-coated cell is 75% while that of the uncoated cell is 69%.
- The Cr has good electrical conductivity, strong adhesion to the substrate and high hardness.

ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form

21 December 2012

Accepted 3 January 2013

Available online 13 January 2013

Keywords:

Chromium

Ion sputtering

Lithium ion battery

Silicon monoxide

ABSTRACT

The effects of Cr coating are studied with respect to improving the electrochemical characteristics of carbon-coated silicon monoxide anodes in rechargeable Li cells. The Cr coating is applied by ion beam sputtering. Analyses of the coating are carried out by EDX, SEM, TEM, and EPMA. A coin cell (CR2032) with a carbon-coated SiO_x anode coated with Cr and a lithium cobalt oxide (LCO) cathode is assembled in an argon-filled glove box. The charged capacity of the Cr-coated SiO_x-C/LCO cell is 1127 mAh g⁻¹ in the 1st cycle at 0.1 C, while that of the uncoated SiO_x-C/LCO cell is 956 mAh g⁻¹. In addition, the Cr-coated SiO_x-C/LCO cell has a discharged capacity of 733 mAh g⁻¹, which is higher than that of the uncoated cell (635 mAh g⁻¹). Furthermore, the discharge capacity retention ratio (100th:2nd) of the Cr-coated cell is 75% while that of the uncoated cell is 69%. The rate capability of the Cr-coated cell is superior to that of the uncoated cell. Cr has good electrical conductivity, enabling more Li ions to be stored in the Cr-coated cell than in the uncoated cell. Investigations into the improved electrochemical characteristics are carried out through the analyses of impedance, voltage profile, and cycle data.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Si anodes represent one of the most suitable types of anode for high-energy Li ion batteries. The theoretical capacity of a Si anode is approximately 4200 mAh g⁻¹, which is more than 10 times higher than that of graphite [1]. However, Si electrodes were found to undergo significant volume changes in cycling. This characteristic causes a drastic fall in their charge/discharge capacity in a long cycle, placing a constraint on the use of Si in Li ion batteries [2–6].

To overcome this problem, carbon-coated SiO_x has been used as an alternative anode material [7–9]. As this material has a high capacity, which is theoretically 1200 mAh g⁻¹, long cycle retention and low charge/discharge potential [10–15] are possible. However,

carbon-coated SiO_x is not completely free of the volume expansion problem, because of which its capacity cannot be fully utilized, especially at high current densities [16]. To solve this problem, we applied a uniform coating of Cr on the surface of a SiO_x-C electrode. Cr has good electrical conductivity, and the Cr coating may impart desirable properties such as strong adhesion to the substrate, high hardness, and excellent wear and corrosion resistance [17–21]. Cr was coated on the SiO_x-C electrode by the ion beam sputtering method [22] to improve the electrochemical characteristics of the SiO_x-C electrode. It was found that the electrochemical cycle capacity increased and better cycle properties were achieved.

2. Experimental

2.1. Fabrication of electrodes

In order to prepare the SiO_x-C electrode, SiO_x (Aldrich, USA, diameter about 10 μm) and spherical natural graphite (Alfa aesar,

* Corresponding author. Tel.: +82 2 3290 3274; fax: +82 2 928 3584.
E-mail address: wyyoon@korea.ac.kr (W.Y. Yoon).

diameter 20 μm) was ball milled and mixed in the ratio of 1:1 by weight. The weight ratio of balls to materials was 5:1 and the milling time was 30 min at 1200 rpm. The composition of the composite material was confirmed by SEM and EDX.

The electrodes were produced by the casting method with 90 wt% of $\text{SiO}_x\text{-C}$ and 10 wt% of PVdF (Aldrich, USA) as a binder, which were dissolved in *N*-methyl-2-pyrrolidone to form a slurry. The slurry was cast into a piece of copper foil of uniform thickness (50 μm). The electrode was vacuum dried at 120 $^\circ\text{C}$ for 3 h and compressed by the roller. Then, Cr was deposited on the electrode surface by ion beam (Dongwoo Surface Tech Co., Ltd., Republic of Korea.) sputtering (Fig. 1). The thickness of the Cr coating was 40–50 nm. This was confirmed with SEM, field emission (FE) TEM (JEM-2100F, JEOL), EDX, and EPMA (JXA-8500F, JEOL). The TEM sample was prepared by focused ion beam milling.

2.2. Test cell assembly

The coin cell (CR2032) was assembled in an argon-filled glove box. Holes with 16 Φ (2.01 mm^2) were punched in the anode (the coating weight was 3.76 mg cm^{-2}). The electrolyte used was a 1 M LiPF_6 solution with an EC:DEC volume ratio of 1:1 (Solbrain, Republic of Korea). The cathode material was lithium cobalt oxide [LCO] Samsung SDI, Republic of Korea], which was punched at 14 Φ (1.54 mm^2 , the thickness of electrode was 100 μm and the coating weight was 27.1 mg cm^{-2}). The assembled cell was aged for 24 h at 40 $^\circ\text{C}$. The capacity of anode was 6.95 mAh, and cathode was 6.89 mAh. It shows that the two electrodes were balanced.

Electrochemical tests were performed galvanostatically using a WBCS 3000 instrument (WonATech Inc., Republic of Korea). The voltage cut-off range in a charging/discharging cycle was 2.75–4.3 V and the C-rate was 0.1 C. The cell was also tested at different C-rates to investigate its rate capabilities. The voltage profiles, cycle performance data, and impedance (measurement were taken at frequencies 10^{-2} to 10^5 Hz in AC amplitude of 5 mV, SOLATRON SI1280B) data of uncoated $\text{SiO}_x\text{-C}$ and Cr-coated $\text{SiO}_x\text{-C}$ electrodes were also compared.

3. Results and discussion

The Cr coating on the $\text{SiO}_x\text{-C}$ electrode was observed by EPMA, high-resolution TEM, SEM, and EDX. Both Fig. 2a and b show EDX

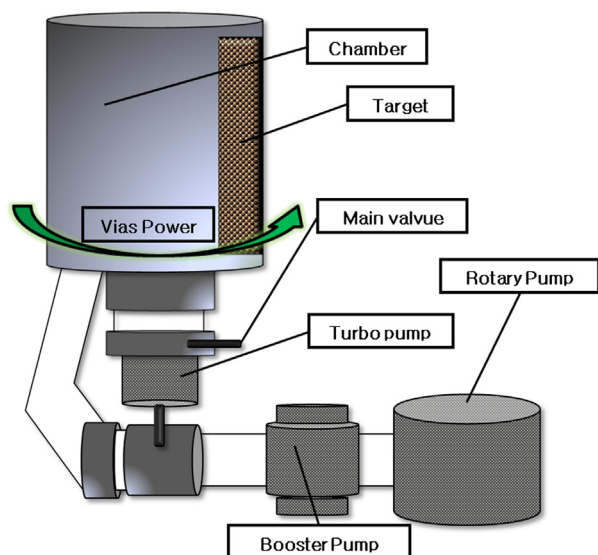


Fig. 1. Sputtering schematic for Cr coating.

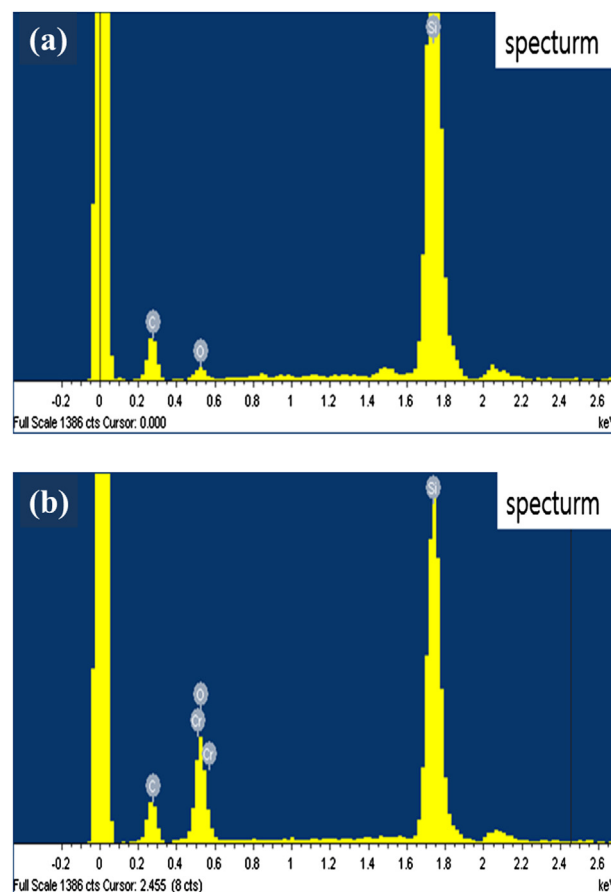


Fig. 2. EDX data for (a) uncoated $\text{SiO}_x\text{-C}$ and (b) Cr-coated $\text{SiO}_x\text{-C}$ electrode.

data which were observed by the surface of uncoated $\text{SiO}_x\text{-C}$ and Cr-coated $\text{SiO}_x\text{-C}$. It shows that there was difference between Fig. 2a and b at range of 0.4–0.6 keV, which range was defined by the Cr. The EPMA data shown in Fig. 3 confirm that Cr was coated uniformly on the surface of the $\text{SiO}_x\text{-C}$ electrode. The FE-TEM image also confirms the Cr coating on the electrode (Fig. 4). The coating thickness was approximately 40–50 nm.

The voltage profiles of the two electrodes are compared in Fig. 5. The first charge and discharge capacities of the uncoated $\text{SiO}_x\text{-C}$ electrode were found to be 956 mAh g^{-1} and 636 mAh g^{-1} , respectively, at 0.1 C. The corresponding values for the Cr-coated $\text{SiO}_x\text{-C}$ electrode were 1127 mAh g^{-1} and 733 mAh g^{-1} , respectively. The high initial capacities for the Cr-coated electrode may be explained by the high electrical conductivity of Cr, which enables the electrode to receive a greater number of Li ions as well as transfer them faster than the uncoated $\text{SiO}_x\text{-C}$ electrode [23].

The specific capacities at 0.1 C over 100 cycles are shown in Fig. 6. With the exception of the first cycle, there is no large difference between the specific capacities of uncoated and Cr-coated $\text{SiO}_x\text{-C}$. However, after the 20th cycle, the difference between the two increases and the Cr-coated $\text{SiO}_x\text{-C}$ electrode demonstrates a higher capacity. The capacity retention efficiency of the Cr-coated $\text{SiO}_x\text{-C}$ electrode from the second to the 100th cycle is 75% (Table 1). This efficiency is superior to that of the uncoated $\text{SiO}_x\text{-C}$ electrode, which has a capacity retention of 69% (the first cycle capacity is ignored in the capacity retention calculation because both SiO_x electrodes exhibit large irreversible capacity loss at the first cycle).

The morphologies of both electrodes after 100 cycles are compared in Fig. 7. The $\text{SiO}_x\text{-C}$ particles in the uncoated electrode bulge

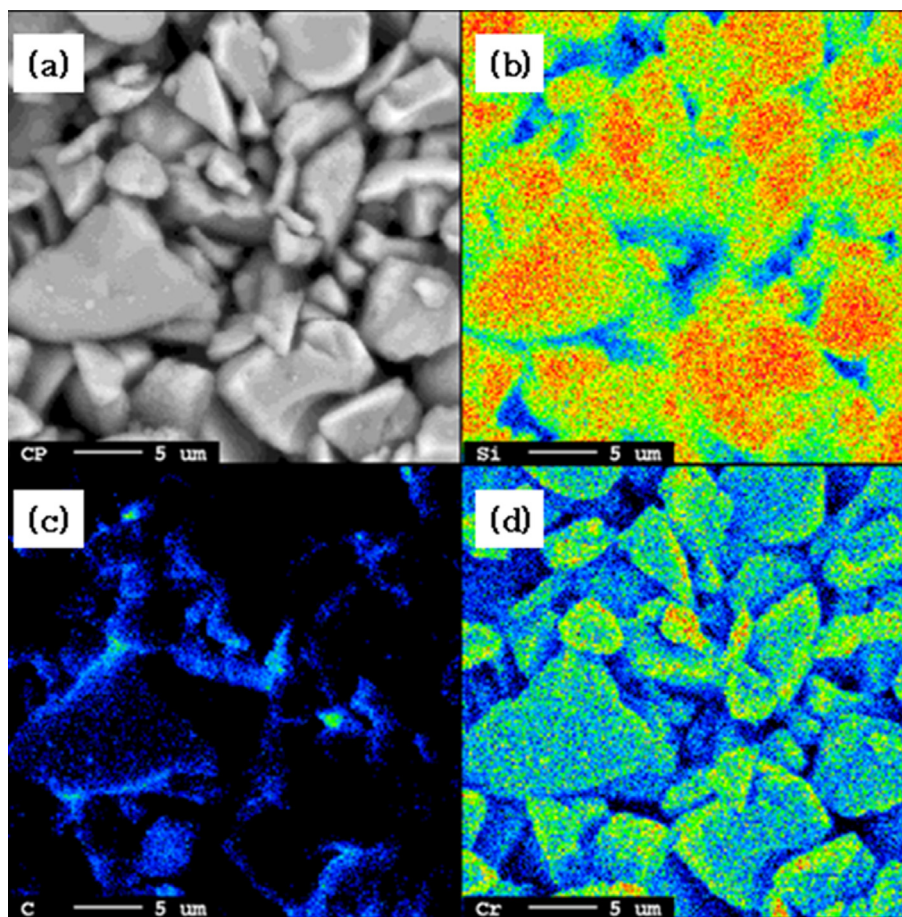


Fig. 3. (a) SEM image of Cr-coated $\text{SiO}_x\text{-C}$ and EPMA measurement results of (b) Si, (c) graphite, and (d) Cr.

distinctly and the surfaces appear to have reacted with the electrolyte (Fig. 7a). However, the morphology of which the Cr-coated $\text{SiO}_x\text{-C}$ particles shows that they have retained their initial shape and their surfaces appear relatively smooth (Fig. 7b). Because the Cr coating enabled the $\text{SiO}_x\text{-C}$ particles to adhere strongly to the substrate, preventing further reaction with the electrolyte, the morphology change in the $\text{SiO}_x\text{-C}$ electrode could be suppressed over long cycles.

In order to better understand the effect of Cr coating, we changed the C-rate (five cycles each at 0.1 C, 0.2 C, 0.5 C and 1.0 C). The observations are given in Fig. 8, which shows that the Cr-coated $\text{SiO}_x\text{-C}$ electrode has a higher capacity for overall current density. Compared with the data for 0.1 C and 0.2 C, the 0.5 C data show greater capacity difference, thus proving that Cr is more effective at a high current density.

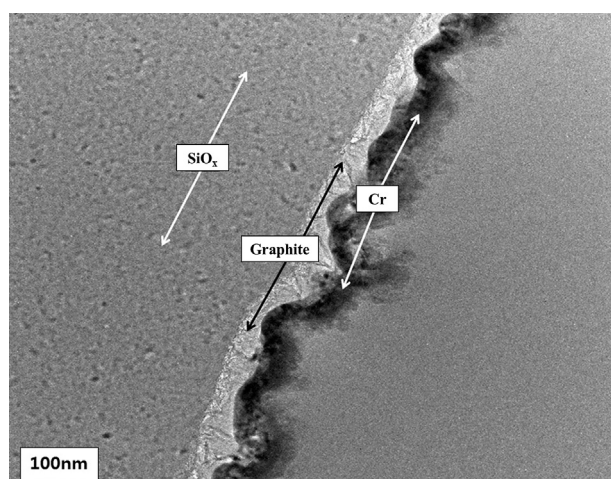


Fig. 4. Field emission TEM image of Cr-coated $\text{SiO}_x\text{-C}$ electrode.

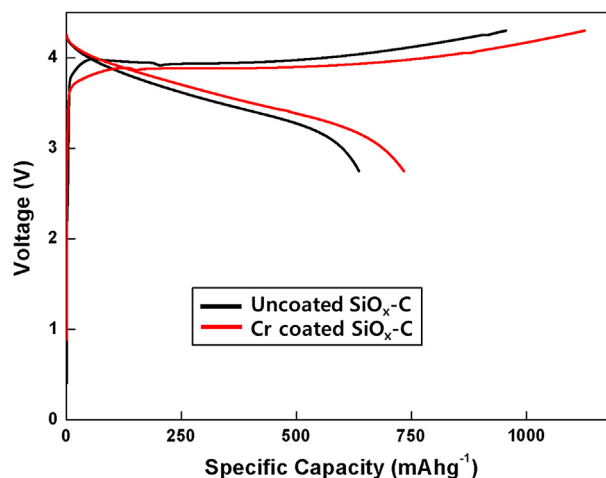


Fig. 5. First cycle voltage profiles for uncoated and Cr-coated $\text{SiO}_x\text{-C}$ electrodes at 0.1 C and cut-off voltage range of 2.75–4.3 V.

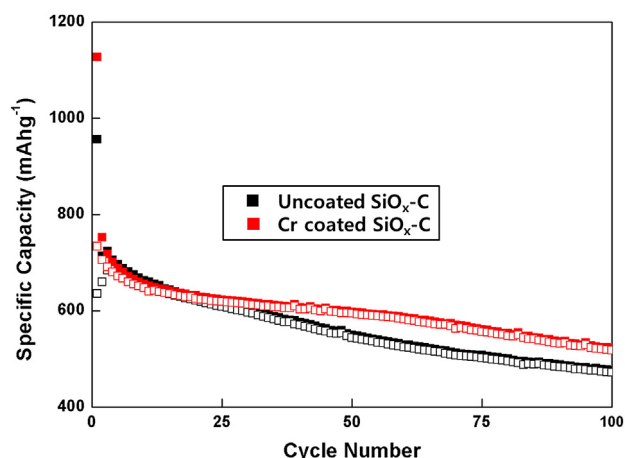


Fig. 6. Charge/discharge capacity profiles for uncoated and Cr-coated $\text{SiO}_x\text{-C}$ electrodes at 0.1 C and cut-off voltage range of 2.75–4.3 V over 100 cycles.

Table 1

Comparison of capacity retention efficiency of the uncoated and Cr-coated $\text{SiO}_x\text{-C}$ electrodes at 0.1 C for 2–100 cycles.

	Uncoated $\text{SiO}_x\text{-C}$ /lithium cobalt oxide electrode	Cr coated $\text{SiO}_x\text{-C}$ /lithium cobalt oxide electrode
2nd discharge capacity	684 mAh g^{-1}	690 mAh g^{-1}
100th discharge capacity	471 mAh g^{-1}	517 mAh g^{-1}
Capacity retention ratio	69%	75%

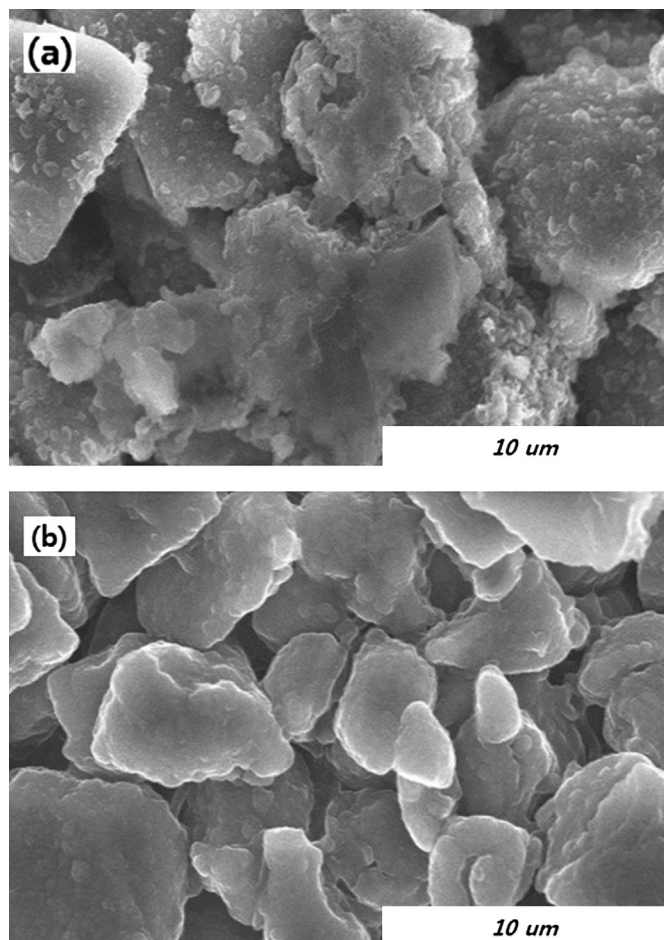


Fig. 7. SEM image of (a) uncoated $\text{SiO}_x\text{-C}$ and (b) Cr-coated $\text{SiO}_x\text{-C}$ after 100 cycles at 0.1 C.

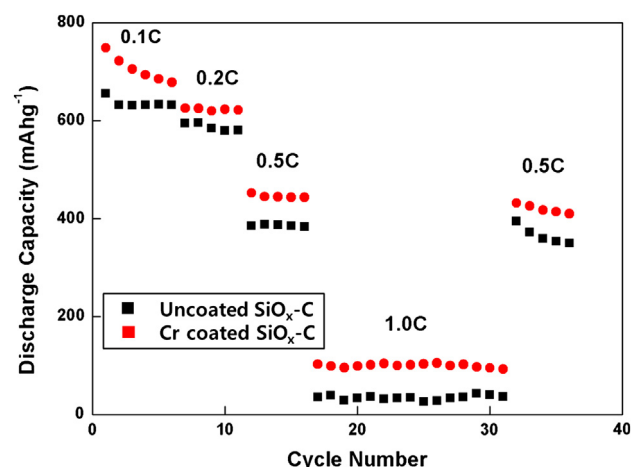


Fig. 8. Charge/discharge capacity profiles for the uncoated and Cr-coated $\text{SiO}_x\text{-C}$ electrodes at 0.1/0.2/0.5/1.0 C and cut-off voltage range of 2.75–4.3 V for five cycles.

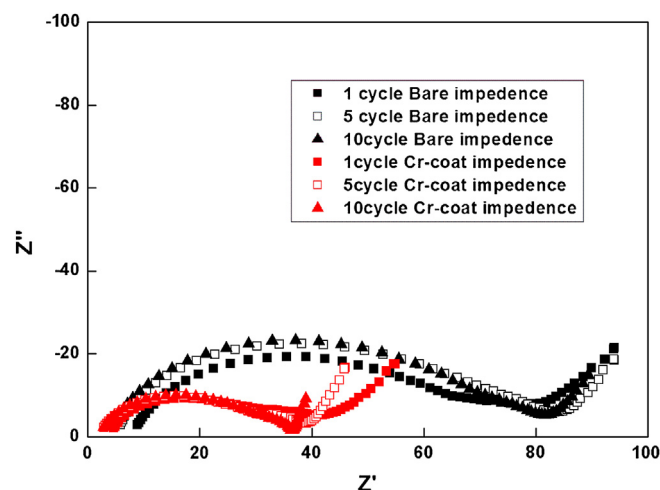


Fig. 9. Impedance data for the uncoated and Cr-coated $\text{SiO}_x\text{-C}$ electrodes (measured after 1, 5, and 10 cycles).

The Cr coating imparts high electrical conductivity to the $\text{SiO}_x\text{-C}$ electrode. This phenomenon was confirmed by impedance data (Fig. 9), which were estimated after the 1st, 5th, and 10th cycles of the Cr-coated and uncoated $\text{SiO}_x\text{-C}$ electrodes. The radius of the first semicircle of the Cr-coated electrode is lower than that of the uncoated $\text{SiO}_x\text{-C}$ electrode for every cycle. This demonstrates that the resistance of the charge-transferring interface of the Cr-coated cell is lower because of the high electrical conductivity of the Cr coating. Thus, Cr may be considered to be an effective coating material for improving the electrochemical properties of a SiO_x electrode.

4. Conclusions

An anode composed of carbon-coated SiO_x and PVdF binder was uniformly coated with Cr by ion beam sputtering. The Cr coating was found to improve the electrochemical performance of the electrode. The first charge capacity of the coated anode was 1127 mAh g^{-1} at 0.1 C, while that of the uncoated electrode was 956 mAh g^{-1} . The discharge capacity retention ratio (100th:2nd) of the Cr-coated cell was 75% while that of the uncoated cell was 69%. The Cr-coated electrode displayed a higher capacity than the uncoated electrode at all evaluated C-rates (0.1 C, 0.2 C, 0.5 C, and

1.0 C). The higher electrical conductivity and superior mechanical properties of the Cr coating resulted in the higher initial capacity, capacity retention and rate capability of the electrode. In addition, the Cr coating may impart desirable properties to the electrode such as strong adhesion to the substrate, high hardness, and excellent wear and corrosion resistance. The superior mechanical properties of the Cr coating allow it to effectively control the volume changes in a SiO_x electrode.

Acknowledgments

This study was supported by the National Research Foundation of Korea (NRF) and funded by a grant from the Korean government (MEST) (2011-0028757).

The microstructures of the samples were observed by TEM at Korea Basic Science Institute, Seoul Center.

The electrode was coated with Cr by ion sputtering deposition at Dongwoo Surface Tech Co., Ltd.

References

- [1] M.N. Obrovac, L. Christensen, *Electrochem. Solid State Lett.* 7 (2004) A93–A96.
- [2] C.K. Chan, H. Peng, G. Liu, K. Mclwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008) 31–35.
- [3] L.-F. Cui, Y. Yang, C.-M. Hsu, Y. Cui, *Nano Lett.* 9 (2009) 3370–3374.
- [4] M.-H. Park, M.G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui, J. Cho, *Nano Lett.* 9 (2009) 3844–3847.
- [5] Y.M. Lee, J.Y. Lee, H.-T. Shim, J.K. Lee, J.-K. Park, *J. Electrochem. Soc.* 154 (2007) A515–A519.
- [6] M. Winter, J.O. Besenhard, *Electrochim. Acta* 45 (1999) 31.
- [7] H.Y. Lee, S.M. Lee, *Electrochem. Commun.* 6 (2004) 465–469.
- [8] H. Chen, Y. Xiao, L. Wang, Y. Yang, *J. Power Sources* 196 (2011) 6657–6662.
- [9] K.B. Kang, H.S. Lee, D.W. Han, G.S. Kim, D.H. Lee, G.H. Lee, Y.M. Kang, M.H. Jo, *Appl. Phys. Lett.* 96 (2010) 053110.
- [10] M. Mamiya, H. Takei, M. Kikuchi, C. Ueda, *J. Cryst. Growth* 229 (2) (2001) 457.
- [11] K. Tahara, F. Iwasaki, T. Tamachi, T. Sakai, in: *The 38th Battery Symposium in Osaka*, 1997, p. 179.
- [12] J.R. Dahn, S. Trussler, T.D. Hatchard, A. Bonakdarpour, J.R. Mueller-Neuhaus, K.C. Hewitt, M.D. Fleischauer, *Chem. Mater.* 14 (2002) 3519.
- [13] M.D. Fleischauer, T.D. Hatchard, G.P. Rockwell, J.M. Topple, S. Trussler, J.R. Dahn, *J. Electrochem. Soc.* 150 (2003) 1465.
- [14] V.K. Cumyn, M.D. Fleischauer, T.D. Hatchard, J.R. Dahn, *Electrochem. Solid State Lett.* 6 (2003) 15.
- [15] I.W. Seong, W.Y. Yoon, *J. Power Sources* 195 (2010) 6143.
- [16] A. Guerfi, P. Charest, M. Dontigny, J. Trottier, M. Lagace, P. Hovington, A. Vijh, K. Zaghbi, *J. Power Sources* 196 (2011) 5667.
- [17] P.K. Gogna, K.L. Chopra, *Thin Solid Films* 63 (1979) 18379.
- [18] G.A. Lausmann, *Surf. Coat. Technol.* (1996) 86996.
- [19] C.A. Huang, W. Lin, M.J. Liao, *Corros. Sci.* 48 (2006) 46006.
- [20] J. Wilden, J.P. Bergmann, S. Jahn, S. Knapp, F. van Rodijnen, G. Fischer, *J. Therm. Spray Technol.* 16 (2007) 5.
- [21] T. Isihara, M. Nakasu, M. Yoshio, H. Nishiguchi, Y. Takita, *J. Power Sources* 146 (2005) 161–165.
- [22] H. Umehara, S. Terauchi, M. Takaya, *Mater. Sci. Forum* (2000) 350.
- [23] N.A. Hamid, S. Wennig, S. Hardt, A. Heinzl, C. Schulz, H. Wiggers, *J. Power Sources* 216 (2012) 76–83.